Synopsis of Ph.D research Work

Title of Proposed thesis

Studies on Chemical Sensing of Various Substances by Different Luminescent Molecules and Materials

by

ABIR MAJI

ROLL NO: C.W.(SIK)-Chem-14

Regn. No.- 1776 of 2015-16

DEPARTMENT OF CHEMSIRTRY

SIKSHA-BHAVANA (INSTITUTE OF SCIENCE)

VISVA-BHARATI, SANTINIKETAN, 731235

WEST BENGAL

Origin of research problem:

The chemical Sensing application is widely used in industrial process, global security and aerospace. The chemical structure of sensor should be small in size, robust and required very small volume of sensing materials or molecules.[1] The luminescent sensing is accurate method for detecting chemical concentration and differentiating among chemicals. Chemical sensing applications ranging from sensing of toxic chemicals to bio-molecules. It is useful technique that is method of low cost, fast response time and greater accessibility. Chemical sensor has been investigated as a low cost and alternative laboratory method but the chemical sensor has been plagued with the problem with like (a) ***reproducibility*** that is inconsistent response to the some chemical sensing over times, (b) ***selectivity*** that is difficulty in differentiating among chemicals**,** (c) ***sensitivity*** that is difficulty in detecting low concentrations of particular chemicals and (d) ***stability*** that is difficulty in detecting chemicals of interest across changes in ambient conditions. Chemical sensing systems that overcome some or all of these problems have various difficulties in keeping manageable level for the corresponding particular sensing applications. However, some progress has been made in the research community balance between cost and robustness of viable chemical sensing application. Most chemical sensors are able to detect concentration reasonably well at medium to high concentrations.

Objective of work:

(1) Synthesis of *Luminescent* Coordination Polymers (***CPs)***, Metal Organic Frameworks(*MOFs*) of d -block, p-block, s-block and rare earth elements.

(2) Synthesis of metal oxides by MOFs and CPs as precursor.

(3) Synthesis of organic dyes derivative like Coumarin, Rhodamines, Pyrene etc.

(4) Characterization of synthesized sample with Single Crystal XRD, PXRD, NMR, UV, IR, TGA etc.

(5) Chemical Sensing application.

(6) Detailed study of Sensing Mechanism.

Methodology:

Hydro thermal and Solvo-tharmal Synthesis of Metal-Organic Compound (MOCs)s:

Typically coordination polymers (CPs) and Metal organic Frameworks (MOFs) is synthesized by Solvo-thermal and Hydra-thermal method. Metal and ligands are mixed with definite ratio in Teflon coated autoclave for 3 to 7 days. Here solvent is added and pH is maintained by strong base.

coordination polymers (CPs) and Metal organic Frameworks (MOFs) sensors have shown excellent potential as chemical sensors for detecting a wide range of molecules such as nitro-explosive, pesticide, small molecules, bio-molecule and ions (Captions, anions). MOFs are new class of coordination polymers (CPs) that are crystalline Inorganic-Organic Hybrid materials constructed from metal ions or clusters bridged by organic ligands to form one-, two- or three-dimensional infinite networks.[2] MOFs are becoming one of the most rapidly developing fields in chemical and material sciences and emerging as an important family of porous materials not only because of their intriguing network topologies[3] but also due to their exploitable properties for potential applications such as gas adsorption and separation,[4] catalysis,[5] luminescence,[6] sensing,[7] proton conduction[8], etc. [9] Their crystalline nature, high and permanent porosity, uniform pore sizes, extraordinary surface areas, finely tunable pore surface properties, and potential scale to

industrial application for further study.[10] The structure and functionality rely strongly on either the two components or the nature and type of connection between them. Not surprisingly, the design of MOFs quickly evolved into these of conformationals rigid organic ligands associated with the secondary building units (SBUs) or supra-molecular building blocks (SBBs).

Synthesis of derivatives of organic dyes:

Synthesis of dye derivative is done by the reflux method.

Luminescence sensing:

Luminescence is an emission of ultraviolet, visible or infrared photons from an electronically excited species. Fluorescence and phosphoresces are the particular case of luminescence. The mode of excitation is adsorption of photons which brings the absorbing species into electronically excited state. The emission of photons accompanying de-excitation is called photoluminescence (Fluorescence, Phosphorescence and delayed Fluorescence).

Luminescent Sensor of ion and molecules:

The design of fluorescent sensors is of major importance because of the high demand in analytical chemistry, clinical biochemistry, medicine, the environment, etc. Numerous chemical and biochemical analytes can be detected by fluorescence methods: nitro-explosive, pesticide, small molecules, bio-molecule and cations (H^+, Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+}, Cd^{2+},

etc.), anions (halide ions, citrates, carboxylates, phosphates, etc.), neutral molecules (sugars, e.g. glucose, etc.) and gases (O_2, CO_2 , NO, etc.).

Mechanism of Luminescent sensing:

Principle of FRET:

In the process of FRET, initially a donor fluorophore (D) absorbs the energy due to the excitation of incident light and transfer the excitation energy to a nearby chromophore, the acceptor (A)

$$D + h\nu \rightarrow D^*$$

$$D^* + A \rightarrow D + A^*$$

$$A^* \rightarrow A + h\nu$$

Photoinduced intramolecular charge transfer (ICT):

Excitation of a fluorophore induces the motion of an electron from one orbital to another. If the initial and final orbitals are separated in space, the electronic transition is accompanied by an almost instantaneous change in the dipole moment of the fluorophore. When the latter possesses an electron-donating group (e.g. $-NH_2$, $-NMe_2$, $-CH_3O$) conjugated to an electron-withdrawing group (e.g. >C=O, -CN).

Future prospect:

We have to design the molecules and materials of specific sensing of chemicals like nitro-explosive, toxic ions, pesticides, small molecules, bio-molecule and biomarkers and but there is much room for improvements. The design of luminescence sensors of dye derivatives and metal organic compounds (MOCs) are of major importance because of the high demand in analytical chemistry, clinical biochemistry, medicinal chemistry etc. Numerous chemical and biochemical

analytes can be detected by luminescence methods Integration of application oriented linker design into MOF synthesis could sustain its continuous prosperity. In addition to exploring new MOF structures and their applications, one can always review the thousands of published MOFs structures; most of them have not been studied or thoroughly studied in the application aspect.

Reference:

1. G. W. Hunter, C. C. Liu, and D. B. Makel, in MEMS Handbook, Chap. 22, M. Gad-el-Hak, Editor, CRC Press LLC, Boca Raton, FL (2001).

2. (a) B. F. Hoskins and R. Robson, J. Am. Chem. Soc., 1989, 111, 5962; (b) B. F. Hoskins and R. Robson, J. Am. Chem. Soc., 1990, 112, 1546; (c) B. Moulton and M. J. Zaworotko, Chem. Rev. , 2001, 101, 1629; (d) A. Y. Robin and K. M.Fromm, Coord. Chem. Rev. , 2006, 250, 2127.

3. (a) D. Zhao, D. J. Timmons, D. Q. Yuan and H. C. Zhou, Acc. Chem. Res., 2011, 44, 123; (b) M. O'Keeffe and O. M. Yaghi, Chem. Rev., 2012, 112, 675; (c) H.-L. Jiang, T. A. Makal and H.-C. Zhou, Coord. Chem. Rev. , 2013, 257, 2232; (d) M. Li,D. Li, M. O'Keeffe and O. M. Yaghi, Chem. Rev. , 2013, 114, 1343; (e) Q. Chen, F. Jiang, D. Yuan, G. Lyu, L. Chenand M. Hong, Chem. Sci., 2014, 483.

4. (a) D. M. D'Alessandro, B. Smit and J. R. Long, Angew. Chem., Int. Ed., 2010, 49, 6058; (b) J.-R. Li, Y. Ma, M.C.McCarthy,J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena and H.-C. Zhou, Coord. Chem. Rev. , 2011, 255, 1791; (c) J.-R. Li, J. Sculley andH.-C. Zhou, Chem. Rev. , 2012, 112, 869; (d) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, Chem. Soc. Rev. , 2012, 41, 2308; (e) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R.

Herm, T.-H. Bae and J. R. Long, Chem. Rev. , 2012, 112, 724; (f) S. Chaemchuen, N. A. Kabir, K. Zhou and F. Verpoort, Chem. Soc. Rev. , 2013, 9304; (g) J.-R. Li, J. Yu, W. Lu, L.-B. Sun, J. Sculley, P. B. Balbuena and H.-C. Zhou, Nat. Commun., 2013, 4, 1538; (h) Y. Yan, S. Yang, A. J. Blake and M. Schro¨der, Acc. Chem. Res. , 2013, 47, 296; (i) J. A. Mason, M. Veenstra and J. R. Long, Chem. Sci. , 2014, 5, 32.

5. (a) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, Chem. Soc. Rev., 2009, 38, 1450; (b) L. Ma, C. Abney and W. Lin, Chem. Soc. Rev. , 2009, 38, 1248; (c) Y. Liu, W. M. Xuan and Y. Cui, Adv. Mater., 2010, 22, 4112; (d) M. Yoon, R. Srirambalaji and K. Kim, Chem. Rev., 2011, 112, 1196; (e) A. Dhakshinamoorthy and H. Garcia, Chem. Soc. Rev., 2012, 41, 5262; (f) H. R. Moon, D.-W. Lim and M. P. Suh, Chem. Soc. Rev., 2013, 42, 1807.

6. (a) Q. Zhu, C. Shen, C. Tan, T. Sheng, S. Hu and X. Wu, Chem. Commun., 2012, 48, 531; (b) J. Heine and K. MullerBuschbaum, Chem. Soc. Rev. , 2013, 42, 9232; (c) H.-L. Jiang,D. Feng, K. Wang, Z.-Y. Gu, Z. Wei, Y.-P. Chen and H.C.Zhou, J. Am. Chem. Soc., 2013, 135, 13934; (d) C.-Y. Sun,X.-L. Wang, X. Zhang, C. Qin, P. Li, Z.-M. Su, D.-X. Zhu, G.-G. Shan, K.-Z. Shao, H. Wu and J. Li, Nat. Commun. ,2013, 4, DOI: 10.1038/ncomms3717.

7. L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. VanDuyne and J. T. Hupp, Chem. Rev. , 2012, 112, 1105.

8. (a) T. Yamada, K. Otsubo, R. Makiura and H. Kitagawa,Chem. Soc. Rev., 2013, 42, 6655; (b) M. Yoon, K. Suh,S. Natarajan and K. Kim, Angew. Chem., Int. Ed., 2013,52, 2688.

9. (a) Q.-L. Zhu, T.-L. Sheng, R.-B. Fu, S.-M. Hu, L. Chen,C.-J. Shen, X. Ma and X.-T. Wu, Chem. – Eur. J. , 2011,17, 3358; (b) H. Miyasaka, Acc. Chem. Res. , 2012, 46, 248;(c)J.-K.Sun, P.Wang,Q.-X. Yao, Y.-J. Chen, Z.-H. Li,Y.-F. Zhang, L.-M. Wu and J. Zhang, J. Mater. Chem.

,2012, 22, 12212; (d) M.-S. Wang, C. Yang, G.-E. Wang,G. Xu, X.-Y. Lv, Z.-N. Xu, R.-G. Lin, L.-Z. Cai and G.-C. Guo,Angew. Chem., Int. Ed., 2012, 51, 3432; (e) W. Zhang andR.-G. Xiong, Chem. Rev., 2012, 112, 1163; (f) E. Coronadoand G. Minguez Espallargas, Chem. Soc. Rev., 2013, 42, 1525;(g) Y.-N. Gong and T.-B. Lu, Chem. Commun., 2013, 49, 7711;(h) S.-L. Li and Q. Xu, Energy Environ. Sci., 2013, 6, 1656.

10. H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi,Science, 2013, 341, DOI: 10.1126/science.1230444.